HIGH TEMPERATURE PROTECTIVE

COATINGS FOR REFRACTORY METALS

PROGRESS REPORT NO. 3

PREPARED UNDER CONTRACT NO. NASw-1030

for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

UNION CARBIDE CORPORATION

CARBON PRODUCTS DIVISION

PARMA, OHIO

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I. INTRODUCTION

Under Contract NASw-1030, iridium is being investigated as a protective coating for tantalum, molybdenum, columbium, and tungsten. A detailed description of the program was presented in Progress Report No. 2. This report describes the research effort for the period 1 May 1965 to 31 July 1965.

II. SUMMARY

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The rate of interdiffusion of iridium and tantalum was determined as a function of temperature in the range 1200° to 1600°C. An apparent activation energy of 53.5 kcal/mole was obtained for the overall diffusion process.

Iridium-coated tantalum specimens were subjected to oxidation tests in slow moving air at 1850°C.

Pressure bonded and electrodeposited coatings of iridium on tantalum were subjected to oxidation tests in slow moving air and in an oxygen-methane flame. A 5-mil iridium coat completely protected tantalum from oxidation for 51 hours at 1850°C in slow moving air. The recession rate of the coating was 0.02 mils/hr. No internal oxidation was observed. A 5-mil iridium coat on tantalum was also cycled four times without failure through various

(over)

temperature spans in the range 25° to 1700°C in an oxygen-methane flame.

Preliminary oxidation tests in slow moving air and in an oxygen-methane flame showed early failure for electrodeposited iridium coats on molybdenum, tantalum, and tungsten. Premature failure was due to poor adherence of the coating.

author

III. EXPERIMENTAL

A. Materials

The high purity iridium sheet used in these experiments was obtained from Engelhard Industries, Incorporated. Sheet thicknesses of 0.005, 0.020, and 0.040 inch were used, depending on the specific application.

The tantalum and columbium (1/4-inch diameter rods and 0.020-inch thick sheets) were purchased from the Stellite Division of Union Carbide Corporation. Molybdenum and tungsten sheets (.020 inch) were purchased from the Fansteel Metallurgical Corporation.

B. Sample Preparation

1. Fused Salt Electrodeposition

The electroplating procedure has been described in Progress Reports 1 and 2. During this report period, a method of preparing the surface of the metal has been developed and standardized for use on all the substrate metals. The standardized surface treatment procedure consists of (1) polishing the substrate surface with wet abrasion papers through 600 grit, (2) scrubbing with hot alconox solution, (3) rinsing with distilled water, (4) dipping into a dilute sulfuric acid (7-8 per cent) to insure neutralization of any residual basic solution, (5) washing again with distilled water, and (6) washing with 95 per cent ethyl alcohol. The specimens were dried in air before being placed into the fused salt electroplating bath.

For the chemical compatibility studies, diffusion couples were prepared by electrodepositing a 1.45 mils to 1.65 mils coating of iridium on 3/4 inch x 3/4 inch x 0.020-inch pieces of tantalum. These pieces were then heated *in vacuo* at 1200°C for one-half hour to establish a metal-to-metal bond, and then they were sectioned with a diamond cut off wheel into $^1/_8$ inch x $^1/_4$ inch specimens for further annealing studies.

Iridium coatings ranging from 1.5 to 5 mils thick were electrodeposited on Mo, Ta, and Cb for microbend specimens. The coated pieces, measuring $^3/_4$ inch x $1^1/_8$ inch x 0.025 inch, are to be preheated prior to sectioning for microbend specimens.

Oxidation specimens measuring $^3/_4$ inch x $1^1/_8$ inch x 0.020 inch were also prepared by electrodeposition. Iridium coatings ranging in thickness from 1.5 to 5 mils were deposited on tantalum, columbium, and molybdenum. Most of these oxidation specimens were tested in the "as-deposited" condition; however, one Ir-Mo specimen was preheated for comparison purposes.

2. Pressure Bonding

Vacuum hot pressing techniques were also used to prepare oxidation test specimens in picture-frame type composites (Figures 1a and 1b) and were used to encapsulate tantalum with iridium. Initially, the picture-frame composites consisted of a $^5/_8$ inch diameter x 0.005 inch tantalum disk, sandwiched between two $^3/_4$ inch diameter x 0.005 inch iridium disks with an iridium "picture frame" around the tantalum (Figure 1a). This geometry was later modified to a square composite containing a cylindrical insert (Figure 1b), a design which allowed additional iridium protection at the edges and facilitated suspension of the specimen in the oxidation test apparatus.

The composites were hot pressed at 1200°C at an ambient pressure of less than 0.3 torr. A pressure of 2700 lbs/in^2 was then applied to the composites for one hour. The die and plunger were machined from Union Carbide, Grade ATJ Stock. As many as four composites were hot pressed in one operation by using Union Carbide Grafoil as a separator between each composite.

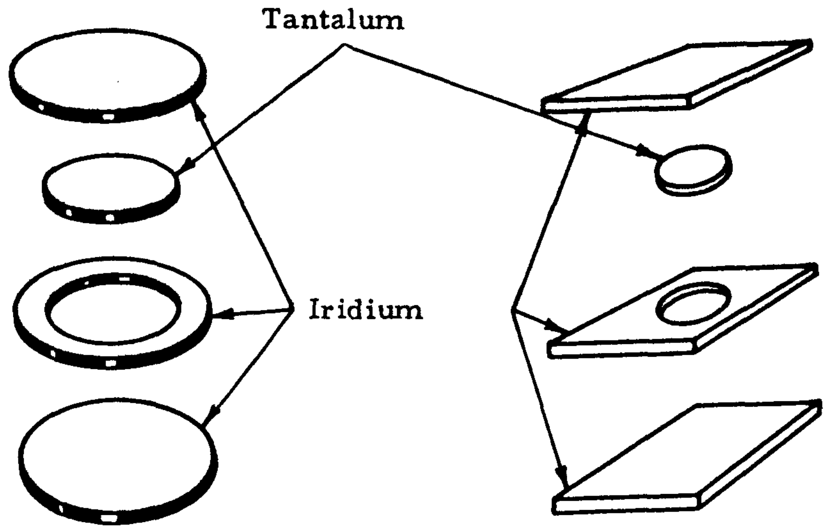


Figure 1a

Figure 1b

Figure 1. Schematic of Picture-Frame Composites Prepared for Pressure Bonding N-7839

3. Roll Bonding

A single attempt was made to roll-bond iridium to tantalum by the Union Carbide Stellite Division. The method used was the same as that described in Progress Report No. 1. The composites were fabricated by sandwiching two pieces of tantalum $^5/_8$ inch x $^5/_8$ inch x 0.020 inch between 5 mil iridium sheets ($^3/_4$ inch x $^3/_4$ inch) and hot-rolling at 1200°C to a 30 per cent reduction in thickness. Both of the roll-bonded composites contained surface cracks and blisters. Since the pressure-bonding experiments provided excellent iridium clad tantalum specimens, we did not order any further roll-bonded material.

C. Sample Evaluation

1. Diffusion Studies

The diffusion couples consisted of tantalum strips coated with electro-deposited iridium. Annealing experiments were carried out in a high temperature vacuum furnace capable of attaining temperatures in excess of 2200°C. An L & N optical pyrometer was used to measure the temperatures.

Diffusion annealing times of 5, 15, 30, and 90 minutes were used to complete the study of diffusion time dependence at 1200°, 1300°, 1400°, 1500°, and 1600°C. The diffusion couples were heated to the desired temperature in 30 to 90 seconds; they were cooled below 1000°C in 30 seconds.

The diffusion zone thickness was determined by measurements from photomicrographs taken at 1000 X and rechecked by direct measurements on a Tukon hardness tester. Each method has an accuracy of ±0.4 micron.

2. Oxidation Tests

Oxidation tests were conducted in an oxygen-methane flame and in an air furnace.

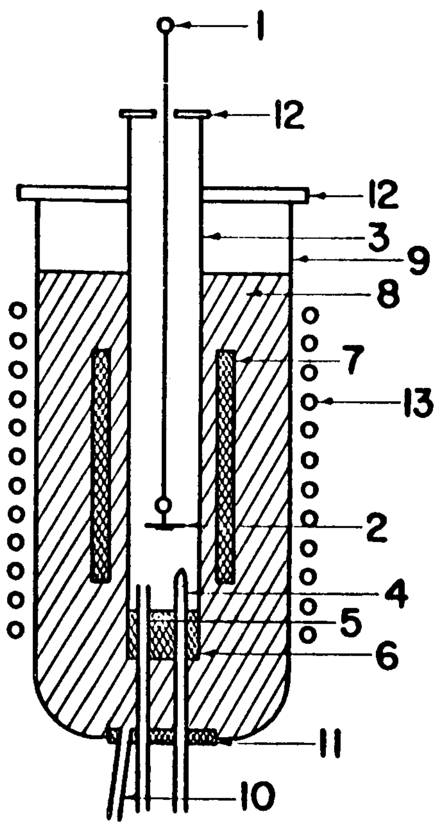
a. Oxygen-Methane Torch Tests

A National Welding Equipment Company Type 3A Blowpipe with an OX-4 tip was used in conducting the oxidation tests in an oxygen-methane flame. The combustion gas flows O_2 and CH_4 were metered with Brooks-Rotomeyer, Sho-Rate-50 Flowmeter to assure an oxidizing environment. A 10-volume per cent excess of oxygen for the combustion of methane was used.

In a typical oxidation experiment, the test sample was supported in a vertical position by a zirconia holder which was slotted to accommodate the thickness of the sample. Graphite baffles were used to protect the flame from room drafts. Surface temperatures were regulated by varying the distance between the torch flame and the test specimen, a distance which ranged from 0.5 to 5 inches. Temperatures were measured with a micro-optical pyrometer by sighting on the side of the specimen which was opposite to the side exposed to the oxidizing flame. No corrections were made for the emissivity of iridium at this time. The true temperature will be obtained from measurements on a small "black body" hole in iridium and comparing the temperature of the hole with the brightness temperature of the adjacent surface. These corrections will be determined for both highly polished and matt iridium surfaces.

b. Air Furnace Tests

A high temperature thermo-gravimetric unit consisting of an Ajax Magnothermic Induction Furnace and an automatic recording balance is being used to conduct oxidation tests in slow moving air (one volume change per minute). The furnace portion of the system is shown in Figure 2. A sample support (1) suspended from an automatic recording balance maintains the sample (2) in the center of an impervious alumina furnace liner tube (3). An alumina thermowell (4) and gas inlet tubes (5) are sealed to the bottom of the furnace liner tube with alumina cement (6). The entire assembly is insulated from a graphite susceptor (7) with graphite felt. A quartz envelope (9) is used to contain the felt. A thermowell, gas inlet, and a furnace flush inlet (10) are inserted in the bottom (11) of the quartz envelope and sealed with Sauereisen cement. Alumina plates (12) are used to enclose the tops of both the furnace liner and quartz envelope. The induction coil (13) is energized with a 6 KW Ajax Magnothermic spark gap converter.



1. Sample support
2. Sample
3. McDanel impervious alumina tube
4. McDanel impervious alumina thermowell
5. McDanel impervious alumina gas inlet tube
6. Morganite 961 alumina cement
7. Graphite susceptor (grade ATJ)
8. Graphite felt (grade WDF) insulation
9. Amersil opaque quartz envelope
10. Quartz furnace flush tube
11. Sauereisen No. 1 cement
12. Sintered alumina plates
13. Ajax Northrup 309 Induction furnace powered with a 6 KW Type "C" converter

Figure 2. 2000°C TGA Furnace N-6317

The automatic recording balance unit consists of an Ainsworth Type BB balance, a Fisher Scientific Company balance recorder, and a Model 75 Fisher Recording Analytical Balance control unit.

c. Coating Recession Rate Determinations

Three methods of determining the recession of iridium were used:

Method I

The first method consisted of measuring the cross-sectional components (coating, substrate, and diffusion zone) by metallographic techniques after oxidation. Figure 3 is a schematic of the specimen after oxidation, showing the iridium, the diffusion zone, and the tantalum thicknesses. The iridium thickness after oxidation was 4.6 mils, 1.2 mils of which are consumed by the diffusion zone. Since the initial iridium thickness was 5 mils, the total iridium consumed by oxidation at 1850°C for 15 hours was 0.4 mils. The iridium recession rate, then, was 0.02 mils/hour.

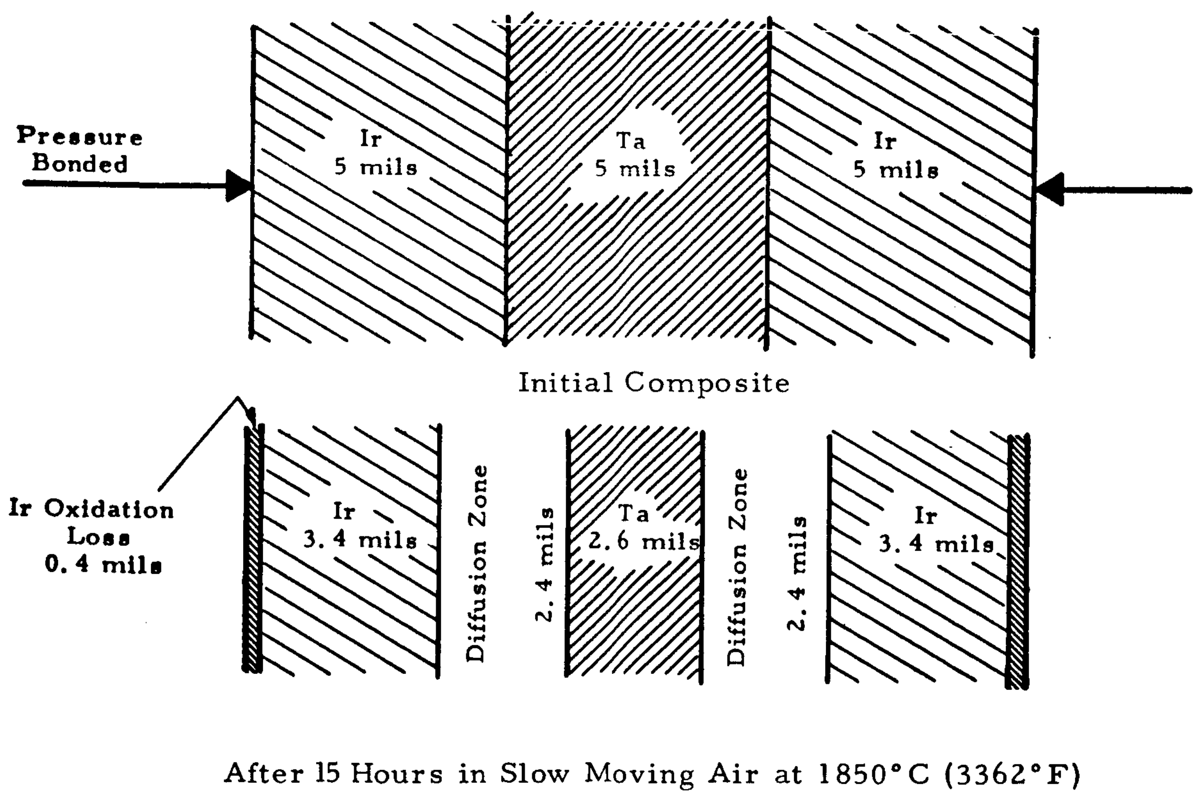


Figure 3. Schematic of Ir-Ta Composite After Oxidation at 1850°C for 15 Hours

Method II

The second method consisted of measuring an iridium portion of the composite where tantalum diffusion did not occur, i.e., at the ends of the composite where only the iridium-iridium bond is present. The thickness of the iridium at the ends of the composite prior to oxidation was 15 mils. After oxidation, the average thickness of 15 measurements was 14.2 mils, corresponding to an iridium decrease of 0.8 mils on each side of the specimen. Again, the iridium recession rate was 0.02 mils/hour for 15 hours.

Method III

The third method consisted of measuring the weight loss of the specimen as a function of time. In this case, the recession rate was determined by considering the weight loss, area, and density of iridium. For example, the weight loss of iridium per cm^2 of surface represents a certain thickness of the metal which can be calculated from the expression,

$$R = \frac{K}{d} \times \frac{390 \text{ mils cm}^2}{1 \text{ cm}^3} = 17.4 \times 10^{-3} K,$$

where R = the recession rate in mils/hour,
K = linear rate constant $mg/cm^2/hr.$,
and d = density of iridium = 22.42 g/cm^3.

A uniform weight loss of 10 mg per hour was obtained for the oxidation of the Ir-Ta composite at 1850°C for 15 hours. Since the surface area was 7.56 cm^2, the recession rate was 1.32 $mg/cm^2/hr$. Using the above equation, R = 0.02 mils/hour.

IV. RESULTS AND DISCUSSION

A. Diffusion Studies

1. The Ta-Ir System

The rate of growth of the diffusion zone thickness for iridium in contact with tantalum was determined at various temperatures in the range 1200°C to 1600°C. The data are summarized in Table I.

TABLE I

HIGH TEMPERATURE DIFFUSION DATA FOR IRIDIUM - TANTALUM COUPLES

Annealing Time Minutes	Total Diffusion Zone Thickness, Microns	Growth Rate* Microns^2/Minute
	1200°C	
30	1.00	0.0523
60	1.50	
120	2.25	
180	3.00	
240	4.00	
	1300°C	
60	3.194	0.177
120	3.873	
180	5.413	
240	6.596	
	1400°C	
5	2.015	0.455
15	2.291	
30	3.619	
90	6.427	
	1500°C	
5	2.828	1.10
15	3.873	
30	6.928	
90	9.801	
	1600°C	
5	3.873	2.84
15	6.427	
30	9.801	
90	15.969	

* Least squares calculation

At the lower temperatures (1200° and 1300°C), annealing times in the range 30 to 240 minutes were used to obtain adequate rate data. Due to the increase in the rate of growth of the diffusion zone thickness with an increase in temperature, annealing times of less than 90 minutes were used for the studies at 1400°, 1500°, and 1600°C. Figure 4 shows a plot of the square of the diffusion zone thickness versus time, demonstrating that the diffusion zone growth rate obeys a parabolic rate law. The straight lines shown in Figure 4 represent a least squares treatment of the data, and the slopes of the lines represent the rate of growth of the diffusion zone at each temperature.

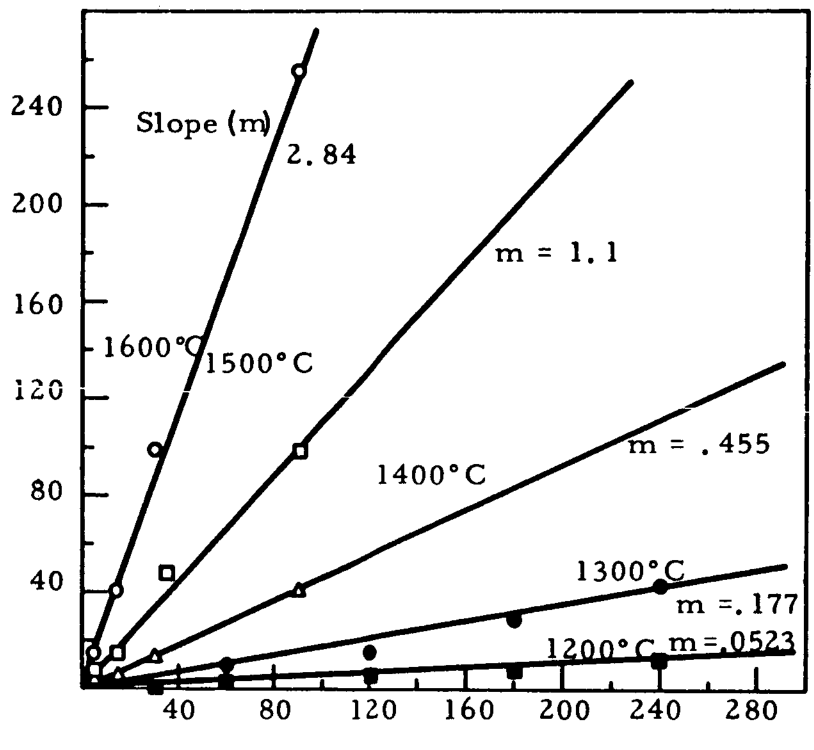


Figure 4. Diffusion Zone Growth as a Function of Time

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From an Arrhenius plot of the data (Figure 5), one obtains an apparent activation energy of 53.5 kcal/mole for the total diffusion process.

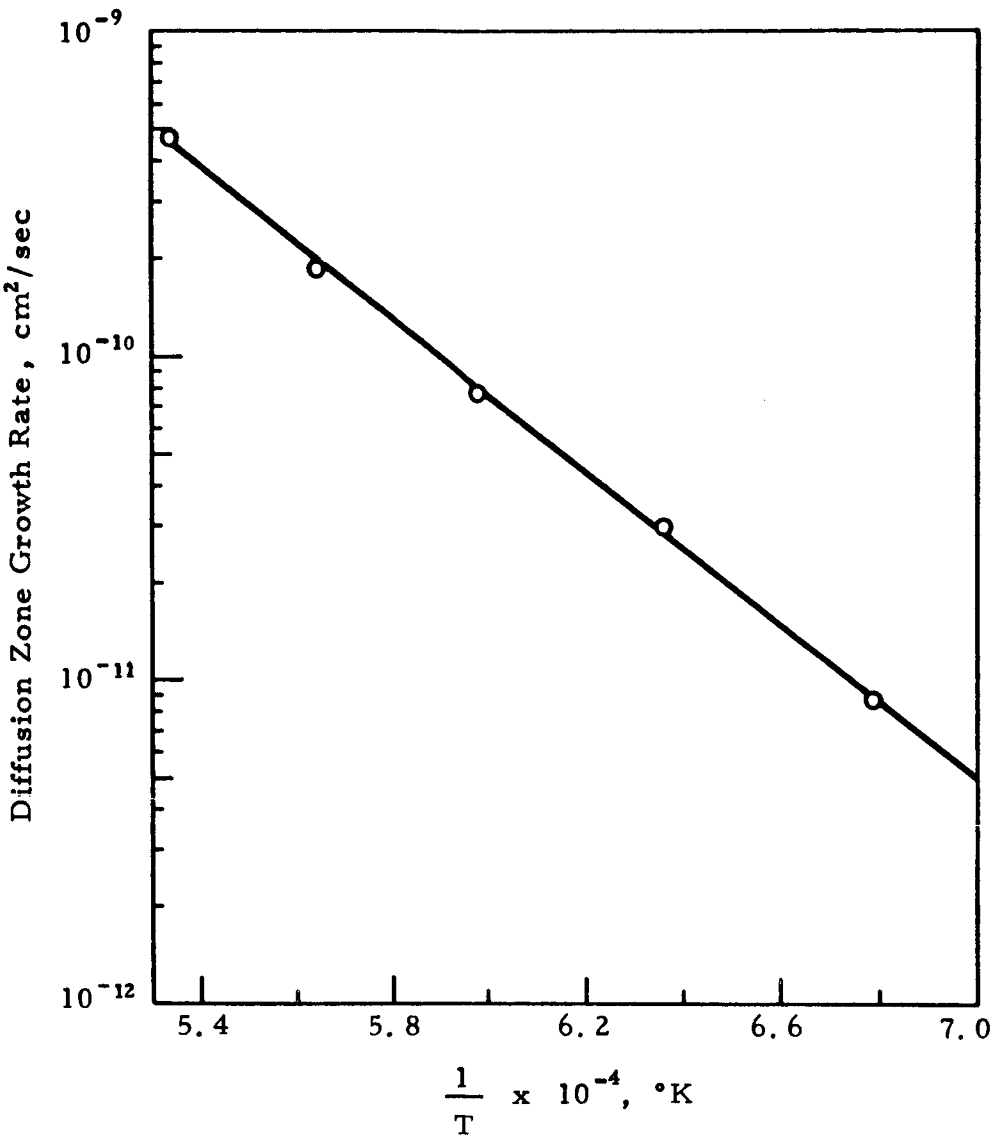

Figure 5. Arrhenius Plot - Diffusion Zone Growth Rate Versus $\frac{1}{T}$ for the Ir-Ta Couple

N-7841

The phase distribution along the diffusion zone is illustrated by the photomicrograph shown in Figure 6. Four phases are discernable between the light layer of iridium and the dark layer of tantalum. The metallographic specimen was electro-etched in HCl at 5 volts D. C. in accordance with the method used by Giésson(1) in his study of the tantalum-iridium binary system. This etching technique stains the σ and α_1 phases, consecutively, then shades the α_2 phase, and, finally the $TaIr_3$. Tentatively, it is believed that these four phases comprise the diffusion zone between tantalum and iridium. Microprobe analyses will be required for confirmation of the phase identification.

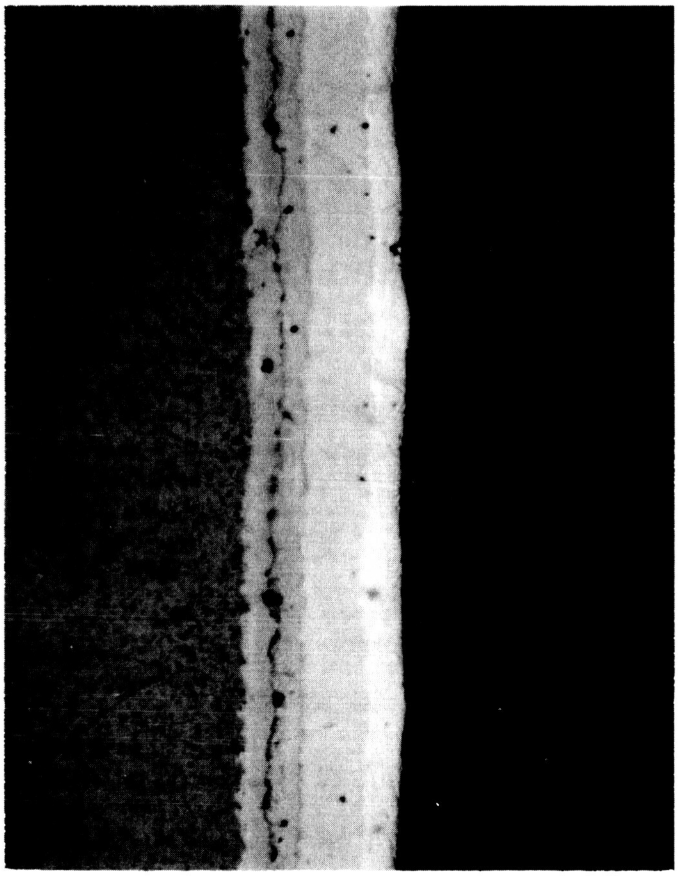

Figure 6. Iridium-Tantalum Diffusion Annealed at 1600°C for Three Hours. Etched 750 X Magnification

N-7858

Additional metallographic examination of the diffusion-annealed specimens are presently being made to obtain the thickness of each individual phase at various annealing times. This information will provide a means for calculating the growth kinetics of each phase and the rate controlling step for the diffusion process.

B. Mechanical Compatibility

The microbend tests used to evaluate the mechanical compatibility have been carried out during this report period, due to the emphasis placed on oxidation tests. Microbend testings will be continued as screening tests to determine if standard bend tests will be performed. Indications are that the standard bend tests will not be required due to the brittle nature of the intermetallics formed at the interface. This conclusion is based on Ta-Ir and Cb-Ir specimens tested to date; however, Mo-Ir and W-Ir specimens will be tested.

C. Fused Salt Electrodeposition

Iridium coatings, having a thickness of 0.001 inch to 0.003 inch were electrodeposited on molybdenum, tantalum, and tungsten from a sodium cyanide-potassium cyanide fused salt electrolyte containing complex iridium-alkali metal cyanide ions. The plated specimens were immersed in a 1:1 HNO_3 to HF solution. The coating was considered to be free of open pores when there was no interaction between the specimen and acid, i.e., no gas evolution from the solution.

The iridium was strongly adherent to molybdenum. A 0.003-inch thick coating of iridium on a 0.25-inch diameter molybdenum rod was plastically deformed and subsequently fractured by several blows with a hammer. The coating cracked only when the substrate was fractured; the iridium could not be peeled off the molybdenum surface, even by prying along the cracks exposing a cross section of the iridium-molybdenum interface.

The deposits on tantalum and tungsten did not exhibit strong bonding between the coating and substrate. Plastic deformation of the coated specimens in these latter two cases always resulted in a separation of the coating from the substrate. Iridium electrodeposited on tantalum or tungsten did form a strong bond when the coated substrate was annealed for one hour at 1500°C.

D. Oxidation Tests

1. Air Furnace Tests

Two pressure-bonded Ir-Ta composites were subjected to oxidation tests in slow moving (one volume change per minute) air at 1850°C. A 5-mil iridium coating provided protection for 51 hours under these test conditions. The average recession rate for this period was 0.02 mils/hour, calculated from weight measurements during the test. Identical conditions were maintained for the second test, discontinued after 15 hours in order that the effects of oxidation on the coating, the substrate, and the diffusion zone might be observed. Metallographic examination of the oxidized specimen revealed no internal oxidation of the Ta substrate or the diffusion zone. The total thickness of the diffusion zone, 2.4 mils, resulted from both the oxidation test and the hot pressing operation. An average recession rate of .02 mils/hour was determined from the test.

Preliminary air furnace oxidation tests were also conducted on molybdenum, tantalum, and tungsten substrates coated with iridium by the fused salt electrodeposition method. These specimens (coating thickness 2.5 to 3 mils) failed at times ranging from 0.1 to 5 hours, a small fraction of the time estimated for the coating life at 1100°C. The causes of the premature failure were, primarily, nonadherence of the coating and the presence of pinholes. Blisters in the coating occurred when specimens were heated in argon and also when they were heated in air.

2. Oxygen-Methane Torch Tests

A specimen of iridium pressure-bonded to tantalum was subjected to the oxygen-methane flame as a test for its resistance to oxidation. The results are listed in Table II. It is again stressed that, at present, we are reporting the uncorrected surface temperaturesfor these experiments.

TABLE II

TEST DATA FOR IRIDIUM PRESSURE BONDED TO TANTALUM*

Cycle No.	Time (min)	Temp., °C**	Remarks
1	5	1325-1350	No signs of failure, air cooled to room temperature
2	5	1400-1425	No signs of failure, air cooled to room temperature
3	5	1600-1625	No signs of failure, air cooled to room temperature
4	20	1650-1700	No signs of failure, air cooled to room temperature

* Coating was a 0.005-inch thickness of iridium
** Temperatures are uncorrected for the emissivity of iridium

During the series of experiments listed in Table II, the iridium coated tantalum did not show any outward signs of substrate oxidation, i.e., tantalum oxide growth. Subsequent metallographic examination again demonstrated complete protection of the tantalum substrate from oxidation. A photomicrograph of the iridium-tantalum specimen showing a cross section of the composite before and after the oxidation cycle is shown in Figures 7a and 7b, respectively. Prior to the oxidation tests, the diffusion zone thickness (Figure 7a) was 16.4 μ, the result of hot pressing and annealing for $\frac{1}{2}$ hour at 1200°C. During the oxidation tests, the diffusion zone thickness increased to 21.7 μ.

The recession of iridium occurs by two mechanisms: (1) loss by oxidation at the outer surface and (2) compound formation at the iridium-tantalum interface. Iridium recession resulting from the series of experiments shown in Table II was determined by measuring the thickness of (a) the tantalum substrate, (b) the total diffusion zone, and (c) the iridium coating before and after oxidation. The total iridium consumption was 1.81 mils. A recession of 1.6 mils was due to oxidation at the coating surface and a 0.2 mil recession was due to interaction at the coating-substrate interface.

Ta -

16.4μ

Ir -

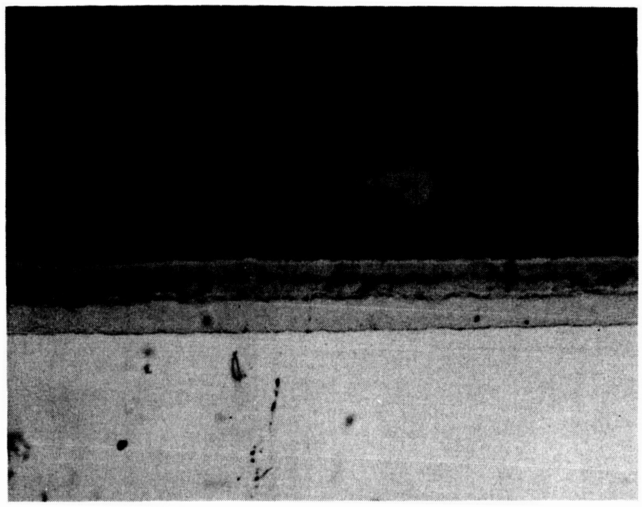

Figure 7a. Ta-Ir as Pressure Bonded Condition
750 X Etched N-7859

Ta -

21.4μ

Ir -

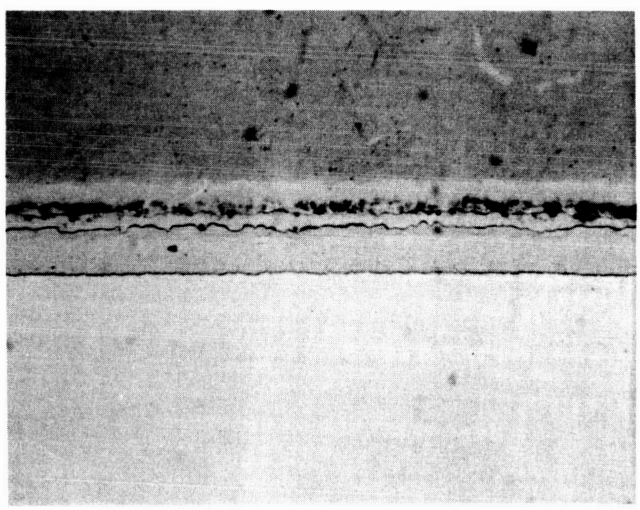

Figure 7b. Ta-Ir Pressure Bonded and Oxidized
750 X Etched N-7860

Figure 7. Ta-Ir Pressure Bonded Composite Before and After an Oxidation Cycle. (1325° to 1700°C)

Preliminary oxidation tests were conducted on electrodeposited iridium coated molybdenum, tantalum, and columbium. The test data are listed in Table III. These tests demonstrate that electrodeposited iridium on molybdenum forms an adherent bond; however, iridium electrodeposited on tantalum and columbium exhibits pinholes and poor adherence.

TABLE 3

OXIDATION TEST DATA - TORCH TESTS ON ELECTRODEPOSITED IRIDIUM COATINGS

Substrate	Coating Thickness (mils)	Sample Condition	Time (min)	Temperature* °C	Remarks
Mo	2.5	as deposited	5	1100-1150	No signs of failure, Cycle 1
		as deposited	5	1300-1350	No signs of failure, Cycle 2
		as deposited	5	1500-1525	No signs of failure, Cycle 3
		as deposited	5	1600-1625	No signs of failure, Cycle 4
		as deposited	5	1700-1725	No signs of failure, Cycle 5
Mo	5.2	as deposited	3	1600	Failure - 1/16-inch diameter hole through coating and substrate
Mo	2.6	annealed 1/2 hr. at 1200°C	60	1050-1100	No sign of failure - air cooled to room temperature, Cycle 1
		annealed 1/2 hr. at 1200°C	60	1300-1350	Failure occurred at end of Cycle 2
Mo	1.9	as deposited	34	1300	Terminated because of Ir corrosion
Mo	1.9	as deposited	5	1125-1150	No failure, Cycle 1
			5	1225-1250	No failure, Cycle 2
			5	1325	Pinhole failure at the end, Cycle 3
Ta	1.3	as deposited	-	---	Failed during heat-up
Ta	1.3	as deposited	3	1200-1400	Failed during heat-up

* Uncorrected for the emissivity of iridium

V. FUTURE PLANS

Oxidation tests will be continued to complete the feasibility studies of iridium as a high temperature protective coating for refractory metals. Emphasis will be placed on oxidation testing of pressure bonded composites consisting of five mil Ir coatings on substrates of W, Mo, and Cb. Values for duration-to-failure life will be obtained in slow moving air at temperatures above 1800°C for each composite. The extent of diffusion and internal oxidation at these high temperatures will be determined by examining a cross section of the oxidized specimens exposed for 15 hours.

Oxygen-methane torch tests will be employed to determine the effects of thermal cycling on the pressure-bonded composites. The mechanical compatibility of iridium with Ta, Mo, Cb, and W will be determined from micro-bend tests performed on specimens in the "as pressure-bonded condition" and, possibly, after oxidizing, if the specimen can be sectioned without destroying the bond.

Additional measurements will be made on Ta-Ir diffusion annealed specimens to obtain the thickness change of each individual phase at various annealing times. Time permitting, a microprobe analysis will be performed to establish positive identification of the four intermetallics present in the Ta-Ir system.

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Carbon Products Division
Parma, Ohio 44130

October 10, 1965

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